

**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371**

022701-978

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.5)

UNASSIGNED 10/009733

INTERNATIONAL APPLICATION NO.  
PCT/FROO/01651INTERNATIONAL FILING DATE  
14 JUNE 2000PRIORITY DATE CLAIMED  
16 JUNE 1999

## TITLE OF INVENTION

CERIUM PHOSPHATE AND/OR LANTHANUM SOL, PREPARATION METHOD AND USE FOR POLISHING

## APPLICANT(S) FOR DO/EO/US

Jean-Jacques BRACONNIER

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☒ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☒ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

## Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

Cover Page of WO 00/76918; PCT/IB/308 and PCT/IB/332



21839

531 Rec'd PCT

17 DEC 2001

U.S. APPLICATION NO. (if known, see 37 C.F.R. 1.5) UNASSIGNED 10/009733	INTERNATIONAL APPLICATION NO. PCT/FR00/01651	ATTORNEY'S DOCKET NUMBER 022701-978
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21. ☒ The following fees are submitted:

CALCULATIONS

PTO USE ONLY

**Basic National Fee (37 CFR 1.492(a)(1)-(5)):**

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... \$1,040.00 (960)

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$890.00 (970)

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$740.00 (958)

International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$710.00 (956)

International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$100.00 (962)

**ENTER APPROPRIATE BASIC FEE AMOUNT =**

\$ 890.00

Surcharge of \$130.00 (154) for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492(e)).

20 ☐ 30 ☐

\$

Claims	Number Filed	Number Extra	Rate
Total Claims	13 -20 =	0	X\$18.00 (966)
Independent Claims	1 -3 =	0	X\$84.00 (964)
Multiple dependent claim(s) (if applicable)			+ \$280.00 (968)

\$ 0.00

\$ 0.00

\$ 0.00

**TOTAL OF ABOVE CALCULATIONS =**

\$ 890.00

Reduction for 1/2 for filing by small entity, if applicable (see below).

+

\$

-

**SUBTOTAL =**

\$ 890.00

Processing fee of \$130.00 (156) for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492(f)).

20 ☐ 30 ☐

+

\$

**TOTAL NATIONAL FEE =**

\$ 890.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 (581) per property

+

\$

**TOTAL FEES ENCLOSED =**

\$ 890.00

Amount to be refunded:

\$

charged:

\$

- a. ☐ Small entity status is hereby claimed.
- b. ☒ A check in the amount of \$ 890.00 to cover the above fees is enclosed.
- c. ☐ Please charge my Deposit Account No. 02-4800 in the amount of \$ to cover the above fees. A duplicate copy of this sheet is enclosed.
- d. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-4800. A duplicate copy of this sheet is enclosed.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Norman H. Stepno  
BURNS, DOANE, SWECKER & MATHIS, L.L.P.  
P.O. Box 1404  
Alexandria, Virginia 22313-1404  
(703) 836-6620

SIGNATURE

TERESA STANEK REA

NAME

30,427  
REGISTRATION NUMBERDECEMBER 17, 2001  
DATE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of )  
 )  
Jean-Jacques BRACONNIER ) Group Art Unit: Unassigned  
 )  
Application No.: UNASSIGNED ) Examiner: Unassigned  
(Corresponds to PCT/FR00/01651) )  
 )  
International Filing Date: 14 JUNE 2000 )  
 )  
For: CERIUM AND/OR LANTHANUM )  
PHOSPHATE SOL, A PROCESS FOR )  
ITS PREPARATION AND USE FOR )  
POLISHING )

PRELIMINARY AMENDMENT

BOX PCT  
Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to examination, please amend the above-captioned application as follows:

IN THE CLAIMS:

Kindly amend the claims as follows:

1. (Amended) A sol, comprising:
  - an aqueous phase;
  - particles of a phosphate of at least one rare earth selected from the group consisting of cerium and lanthanum;
  - an acid other than phosphoric acid, the cerium and lanthanum salts of which are soluble in water.

2. (Amended) A sol as claimed in claim 1, wherein said acid is selected from acids with a  $pK_a$  of at least 3.

3. (Amended) A sol according to claim 1, wherein said acid is selected from the group consisting of nitric acid, acetic acid, formic acid, citric acid and propionic acid.

4. (Amended) A sol according to claim 1, wherein its pH is at least 4.

5. (Amended) A sol according to claim 1, wherein the rare earth phosphate particles are constituted by elementary crystals 5 nm to 20 nm thick and in the range 25 nm to 200 nm in length.

6. (Amended) A process for preparing a sol of a phosphate of at least one rare earth selected from the group consisting of cerium and lanthanum according to claim 1, comprising the following steps:

- mixing a solution of salts of at least one of said rare earths with phosphate ions in a  $PO_4^{3-}$ /rare earth mole ratio of more than 1 with control of the pH of the reaction medium to a value of more than 2;
- then ageing the precipitate obtained if the value of the pH of the reaction medium is in the range 2 to 6;
- separating the precipitate from the reaction medium;

- re-dispersing said precipitate in water;
- adding at least one salt of said rare earth and said acid to the dispersion in a quantity such that the final  $\text{PO}_4^{3-}$ /rare earth mole ratio in the dispersion is equal to 1.

7. (Amended) A process for preparing a sol of a phosphate of at least one rare earth selected from cerium and lanthanum according to claim 1, comprising the following steps:

- continuously introducing, with stirring, a first solution of salts of at least one of said rare earths into a solution containing phosphate ions and with an initial pH of less than 2; the phosphate ions being present in a quantity such that the  $\text{PO}_4^{3-}$ /rare earth mole ratio is more than 1;
- controlling the pH of the reaction medium to a substantially constant value of less than 2 during precipitation;
- separating the precipitate from the reaction medium;
- re-dispersing said precipitate in water;
- adding at least one salt of said rare earth and said acid to the dispersion obtained in a quantity such that the final  $\text{PO}_4^{3-}$ /rare earth mole ratio in the dispersion is 1.

8. (Amended) A process according to claim 6, wherein the pH of the precipitation medium is controlled by adding a basic compound.

9. (Amended) A process according to claim 8, wherein said basic compound is ammonium hydroxide.

10. (Amended) A process according to claim 6, wherein said phosphate ions are in the form of an ammonium phosphate solution.

11. (Amended) A polishing suspension, comprising a sol according to claim 1.

12. (Amended) An anti-corrosion agent comprising the sol according to claim 1.

13. (Amended) An anti-UV agent comprising the sol according to claim 1.

**REMARKS**

Entry of the foregoing amendments are respectfully requested.

Should the Examiner have any questions concerning the subject application, a telephone call to the undersigned would be appreciated.

Respectfully submitted,

BURNS, DOANE, SWECKER & MATHIS, L.L.P.

By: 

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Teresa Stanek Rea  
Registration No. 30,427

P.O. Box 1404  
Alexandria, Virginia 22313-1404  
(703) 836-6620

**Date: December 17, 2001**

**Attachment to Preliminary Amendment dated December 17, 2001**  
**Mark-up of Claims 1-13**

1. (Amended) A sol, [characterized in that it comprises] comprising:
  - an aqueous phase;
  - particles of a phosphate of at least one rare earth selected from the group consisting of cerium and lanthanum;
  - an acid other than phosphoric acid, the cerium and lanthanum salts of which are soluble in water.
2. (Amended) A sol as claimed in claim 1, [characterized in that] wherein said acid is selected from acids with a  $pK_a$  of at least 3.
3. (Amended) A sol according to claim 1 [or claim 2], [characterized in that] wherein said acid is selected from the group consisting of nitric acid, acetic acid, formic acid, citric acid and propionic acid.
4. (Amended) A sol according to [any one of the preceding claims] claim 1, [characterized in that] wherein its pH is at least 4[, more particularly in the range 4 to 6].
5. (Amended) A sol according to [any one of the preceding claims] claim 1, [characterized in that] wherein the rare earth phosphate particles are constituted by elementary crystals 5 nm to 20 nm thick and in the range 25 nm to 200 nm in length.



**Attachment to Preliminary Amendment dated December 17, 2001**  
**Mark-up of Claims 1-13**

6. (Amended) A process for preparing a sol of a phosphate of at least one rare earth selected from the group consisting of cerium and lanthanum according to [any one of claims 1 to 5] claim 1, [is characterized in that it comprises] comprising the following steps:

- mixing a solution of salts of at least one of said rare earths with phosphate ions in a  $\text{PO}_4^{3-}$ /rare earth mole ratio of more than 1 with control of the pH of the reaction medium to a value of more than 2;
- then ageing the precipitate obtained if the value of the pH of the reaction medium is in the range 2 to 6;
- separating the precipitate from the reaction medium;
- re-dispersing said precipitate in water;
- adding at least one salt of said rare earth and said acid to the dispersion in a quantity such that the final  $\text{PO}_4^{3-}$ /rare earth mole ratio in the dispersion is equal to 1.

7. (Amended) A process for preparing a sol of a phosphate of at least one rare earth selected from cerium and lanthanum according to [any one of claims 1 to 5] claim 1, [characterized in that it comprises] comprising the following steps:

- continuously introducing, with stirring, a first solution of salts of at least one of said rare earths into a solution containing phosphate ions and with an initial pH of less than 2; the

**Attachment to Preliminary Amendment dated December 17, 2001**  
**Mark-up of Claims 1-13**

phosphate ions being present in a quantity such that the  $\text{PO}_4^{3-}$   
/rare earth mole ratio is more than 1;

- controlling the pH of the reaction medium to a substantially constant value of less than 2 during precipitation;
- separating the precipitate from the reaction medium;
- re-dispersing said precipitate in water;
- adding at least one salt of said rare earth and said acid to the dispersion obtained in a quantity such that the final  $\text{PO}_4^{3-}$ /rare earth mole ratio in the dispersion is 1.

8. (Amended) A process according to claim 6 [or claim 7], [characterized in that] wherein the pH of the precipitation medium is controlled by adding a basic compound.

9. (Amended) A process according to claim 8, [characterized in that] wherein said basic compound is ammonium hydroxide.

10. (Amended) A process according to [any one of claims 6 to 9] claim 6, [characterized in that] wherein said phosphate ions are in the form of an ammonium phosphate solution[, more particularly mono-ammonium phosphate or di-ammonium phosphate].

**Attachment to Preliminary Amendment dated December 17, 2001**  
**Mark-up of Claims 1-13**

11. (Amended) A polishing suspension, [characterized in that it comprises] comprising a sol according to [any one of claims 1 to 5 or a sol as obtained by the process of any one of claims 6 to 10] claim 1.

12. (Amended) [Use of a sol according to any one of claims 1 to 5 or a sol as obtained by the process of any one of claims 6 to 10, on a substrate as an] An anti-corrosion agent comprising the sol according to claim 1.

13. (Amended) [Use of a sol according to any one of claims 1 to 5 or a sol as obtained by the process of any one of claims 6 to 10, as an] An anti-UV agent comprising the sol according to claim 1.

CERIUM AND/OR LANTHANUM PHOSPHATE SOL, A PROCESS FOR ITS  
PREPARATION AND USE FOR POLISHING

RHODIA CHIMIE

5

The invention concerns a cerium and/or lanthanum phosphate sol, a process for its preparation and its use in polishing.

The development of the electronics industry requires an ever-increasing use of compositions for polishing the various parts such as disks or dielectric components. Such compositions are in the form of suspensions and they have to satisfy a number of characteristics. As an example, they must have a high matter removal rate which stems from their abrasive nature. They must also have the lowest possible defectivity, with "defectivity" meaning the number of scratches on the substrate treated by the composition. A certain selectivity of the composition towards a metal may also be required. Thus the development of such compositions is a complex problem.

Thus there exists a need for such polishing compositions.

The aim of the invention is to provide such compositions and a process for preparing such compositions.

To this end, the sol of the invention is characterized in that it comprises:

- an aqueous phase;
- particles of a phosphate of at least one rare earth selected from cerium and lanthanum;
- an acid other than phosphoric acid the cerium and lanthanum salts of which are soluble in water.

Further, the invention also concerns a process for preparing a sol of a phosphate of at least one rare earth selected from cerium and lanthanum which, in a first implementation, is characterized in that it comprises the following steps: mixing a solution of salts of at least one said rare earth with phosphate ions in a  $\text{PO}_4^{3-}$ /rare earth mole ratio of more than 1 with control of the pH of the reaction medium to a value of more than 2; ageing the precipitate obtained if the value of the pH of the reaction medium is in the range 2 to 6; separating the precipitate from the reaction medium; re-

dispersing said precipitate in water; adding at least one salt of said rare earth to the dispersion and said acid in a quantity such that the final  $\text{PO}_4^{3-}$ /rare earth mole ratio in the dispersion is 1.

In a second implementation of the invention, a process for preparing a sol of a phosphate of at least one rare earth selected from cerium and lanthanum is characterized in that it comprises the following steps: continuously introducing, with stirring, a first solution of salts of at least one said rare earth into a second solution containing phosphate ions and with an initial pH of less than 2; the phosphate ions being present in a quantity such that the  $\text{PO}_4^{3-}$ /rare earth mole ratio is more than 1; controlling the pH of the reaction medium to a substantially constant value of less than 2; separating the precipitate from the reaction medium; re-dispersing said precipitate in water; adding at least one salt of said rare earth and said acid to the dispersion in a quantity such that the final  $\text{PO}_4^{3-}$ /rare earth mole ratio in the dispersion is 1.

Further characteristics, details and advantages of the invention will become more apparent from the following description and non-limiting examples given by way of illustration.

The invention concerns a sol of a rare earth phosphate, the rare earth being cerium or lanthanum, more precisely an orthophosphate with formula  $\text{LnPO}_4$ , Ln designating the rare earth. This orthophosphate is hydrated and has a hexagonal structure. The invention is, of course, applicable to mixed cerium and lanthanum phosphates  $(\text{La,Ce})\text{PO}_4$  and the term "rare earth phosphate" will be used in a general manner in the remainder of the description with the meaning which has just been defined in this paragraph.

Throughout the remainder of the description, the expression "sol" or "colloidal dispersion" of a rare earth phosphate designates any system constituted by fine solid particles of colloidal dimensions based on this phosphate in suspension in a liquid phase, said phosphate also possibly containing residual quantities of bonded or adsorbed ions such as nitrates, acetates, citrates or ammonium. It should be noted that in such dispersions, the phosphate can be either completely in the form of colloids, or simultaneously in the form of ions and in the form of colloids.

The average diameter of the rare earth phosphate particles is generally at most 200 nm. These particles are constituted by an agglomeration of elementary crystals, generally acicular in form, about 5 nm to 20 nm thick and a few tens of nanometres long, in particular in the range about

25 nm to about 200 nm. The average diameter of the particles or colloids is determined by Sedigraph granulometric analysis and the shapes and dimensions of the elementary crystals are determined by electron microscopy.

In one feature of the invention, the sol also contains an acid. This acid is an acid other than phosphoric acid. It is an acid selected from those the lanthanum and cerium salts of which are soluble in water. This acid can in particular be an organic acid. More particularly, this acid can be selected from those wherein the  $pK_a$  is at least 3. Examples which can be cited are nitric acid, acetic acid, formic acid, citric acid and propionic acid. The acid can be present in any form, dissociated or undissociated.

Preferably, the pH of the sol of the invention is at least 4. This pH can in particular be in the range 4 to 6, more particularly between 4.5 and 5.5. The pH of the sol can be fixed at different values depending on the  $pK_a$  of the acid used.

The concentration of the sol can vary between wide limits, for example in the range 0.01 to 2 moles of  $LnPO_4$  per litre.

The process for preparing the sol of the invention will now be described. Two implementations can be employed for the process.

The first implementation corresponds to a process of the type mentioned in European patent application EP-A-0 498 689 the description of which should be referred to.

As indicated above, this first implementation comprises a first step in which a solution of salts of at least one said rare earth is mixed with phosphate ions in a  $PO_4^{3-}$ /rare earth mole ratio of more than 1, controlling the pH of the reaction medium to a value of more than 2.

In particular, suitable rare earth salts are salts which are soluble in aqueous media, such as nitrates, chlorides, acetates, carboxylates or a mixture thereof.

The phosphate ions which are intended to be reacted with the solution of rare earth salts can be supplied by compounds which are pure or in solution, such as phosphoric acid, alkali phosphates or phosphates of other metallic elements producing a soluble compound with the anions associated with the rare earths. The phosphate ions are preferably added in the form of a solution of an

ammonium phosphate which can more particularly be di-ammonium or mono-ammonium phosphate.

The phosphate ions are present in a quantity such that the reaction medium has a  $\text{PO}_4^{3-}$ /rare earth mole ratio of more than 1, advantageously in the range 1.1 to 3.

5 The term "controlled pH" means the pH of the precipitation medium is held at a certain value, which is constant or substantially constant, by adding basic compounds or buffer solutions to the medium. The pH of the medium will thus vary by at most 0.5 pH units about the set value, preferably by at most 0.1 pH unit about this value.

10 The mixture of the solution of the rare earth salt and the phosphate ions produces a precipitate. The precipitate is aged in the precipitation medium, after mixing is complete, for a period which can, for example, be in the range about 15 min to about 10 hours, when precipitation takes place at a pH in the range about 2 to 6. This ageing can produce a product which can be filtered. This ageing step is not necessary when the pH of the precipitation medium is more than 6. However, it can be carried out to further improve the filterability of the precipitate. Ageing can be  
15 carried out at any temperature, for example in the range 15°C to 100°C.

The pH is advantageously controlled by adding a basic compound. Examples of suitable basic compounds which can be cited are metallic hydroxides ( $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Ca}(\text{OH})_2$ , ...) or ammonium hydroxide, or any other basic compound the constituent species of which do not form  
20 any precipitate when added to the reaction medium, by combination with one of the other species contained in the medium, to control the pH of the precipitation medium. A preferred basic compound is ammonia, advantageously used in an aqueous solution.

Precipitation is preferably carried out in an aqueous medium at a temperature which is not critical and which is advantageously in the range from ambient temperature (15°C-25°C) to 100°C. The reaction medium is stirred while precipitation takes place.

25 The precipitate obtained can be separated from the reaction medium by any suitable means, in particular by filtering. It can, for example, be washed with water to eliminate any impurities.

The precipitate is then dispersed in water. Finally, at least one said rare earth salt and said acid other than phosphoric acid are added in a quantity such that the final  $\text{PO}_4^{3-}$ /rare earth mole ratio

in the dispersion is equal to 1. This addition is made with stirring and, optionally, hot. Ageing can be carried out for a period in the range 15 minutes to 1 hour.

At the end of this last step, a dispersion or sol of the rare earth phosphate of the invention is obtained. This sol is stable.

5 The preparation process can also be carried out in accordance with a second implementation which is the preferred implementation. This second implementation corresponds to the process described in European patent application EP-A-0 581 622 the description of which can be referred to.

10 The first step of this process consists of introducing, continuously and with stirring, a first solution of salts of at least one of said rare earth salts into a second solution containing phosphate ions and with an initial pH of less than 2; during precipitation, the pH of the precipitation medium is controlled at a substantially constant value of less than 2.

15 The above description with respect to the first implementation regarding the precipitation parameters, in particular as regards the rare earth salts, the phosphate ions ( $\text{PO}_4^{3-}$ /rare earth mole ratio of more than 1) and controlling the pH is also applicable here.

20 However, a certain order of introducing the reactants must be followed; more precisely, the solution of soluble salts of the rare earth or rare earths must be introduced slowly and continuously into the solution containing the phosphate ions. Further, the solution containing the phosphate ions must initially (i.e., before starting to introduce the solution of rare earth salts) have a pH of less than 2, preferably in the range 1 to 2. Further, while the solution used naturally does not have such a pH, the latter is brought to the suitable desired value either by adding a base (for example ammonia, in the case of an initial solution of phosphoric acid) or by adding an acid (for example nitric acid in the case of an initial solution of di-ammonium phosphate).

25 Next, during introduction of the solution containing the rare earth salt or salts, the pH of the precipitation medium gradually reduces; further, to maintain the pH of the precipitation medium to the desired constant working value, it must be less than 2 and preferably in the range 1 to 2, a basic compound is simultaneously introduced into this medium.



At the end of the reaction, a precipitate is recovered which is treated in the same manner as that described in the case of the first implementation to obtain the sol of the invention.

The invention also concerns a suspension for polishing, comprising a sol as described above or a sol as obtained by the processes described above. This suspension can be used to polish glass, for example in the areas of glass making, glazing, plate glass, television screens, spectacles, or for polishing ceramic materials or other vitreous type materials. More particularly, this suspension can also be used for CMP type polishing in the electronics industry. In this case, it is particularly suitable for polishing metallic substrates used in producing microprocessors, these substrates being produced from copper, aluminium, titanium nitride or tungsten.

In general, in addition to the compound with an abrasive property such as the sol of the invention, such suspensions comprise additives such as a dispersing agent or an oxidising agent.

The sol of the invention can also be used on a substrate as an anti-corrosion agent, for example on metallic substrates and in particular on steel substrates.

The condition of the substrate before the treatment does not require any particular intervention, apart from conventional degreasing and cleaning treatments. The substrates may or may not be pre-oxidised.

Deposition on the substrate can be carried out directly from the sol using conventional coating techniques of the dipping or spraying type, for example.

The substrate must then be heat treated, in particular to eliminate water.

The heat treatment is generally carried out at a temperature of at most 600°C. This temperature can be lower, for example at most 400°C, depending on the nature of the substrates.

Finally, the sol of the invention can be used as an anti-UV agent, for example in plastic materials.

Non limiting examples will now be given.

## EXAMPLE 1

This example concerns the preparation of a cerium phosphate sol of the invention.

Firstly, a 2 mol/l phosphoric acid solution was heated to 60°C and pre-neutralised to a pH of 1.5 by 6 mol/l ammonia. A 2 mol/l cerium nitrate solution was added continuously over 1 hour.

The quantity of solution was determined so as to have a  $\text{PO}_4^{3-}$ /rare earth mole ratio of 1.1. The pH of the reaction medium was adjusted to 1.5 by adding ammonia in a concentration of 6 mol/l. The final concentration of precipitated cerium phosphate was 0.75 mol/l.

The reaction mixture was aged for 30 minutes at 60°C. It was filtered than washed with cold water. It was dried in a Buchner flask for 15 minutes.

The moist phosphate obtained had an excess of  $\text{PO}_4^{3-}$  ions of  $0.6 \times 10^{-3}$  mole/g. 4.5 kg of this phosphate was dispersed in 30 l of deionised water then after stirring, 974 g of cerium acetate was added so that the  $\text{PO}_4^{3-}$ /Ce ratio was brought to 1.

The mixture was allowed to age for 30 minutes at ambient temperature.

The final concentration of the sol was 100 g/l of cerium phosphate; the pH was 4.8.

TEM microscopic analysis showed that the phosphate was in the form of particles constituted by acicular crystals up to 170 nm long and with a width in the range 5 to 20 nm.

### EXAMPLE 2

The procedure of Example 1 was followed until a moist cerium phosphate was obtained with an excess of  $\text{PO}_4^{3-}$  ions of  $0.5 \times 10^{-3}$  mole/g of cerium phosphate with respect to the exact stoichiometry.

189 g of this cerium phosphate was dispersed in 1 litre of deionised water with stirring and at 20°C.

55 g of cerium nitrate in solution was added to this dispersion at 20°C and with stirring, so that the  $\text{PO}_4^{3-}$ /rare earth ratio was brought to 1.

The mixture was aged for 30 minutes at 20°C.

The final concentration of this sol was 110 g/l of cerium phosphate and its pH was 1.4.

### EXAMPLE 3

This example concerns the preparation of a lanthanum phosphate sol of the invention.

Precipitation of the lanthanum phosphate was identical to that of the cerium phosphate of the preceding examples. The moist lanthanum phosphate obtained had an excess of  $\text{PO}_4^{3-}$  ions of  $6.6 \times 10^{-4}$  mole/g of moist lanthanum phosphate with respect to the exact stoichiometry.

170 g of moist lanthanum phosphate was dispersed in 1.1 litres of deionised water with stirring and at 20°C.

24 g of lanthanum acetate  $\text{La}(\text{CH}_3\text{COO})_3 \cdot 1.3\text{H}_2\text{O}$  was added to this dispersion at 20°C and with stirring, so that the  $\text{PO}_4^{3-}$ /rare earth ratio was brought to 1.

The mixture was aged for 30 minutes at 20°C.

The final concentration of this sol was 100 g/l of lanthanum phosphate and its pH was 4.5.

#### EXAMPLE 4

The starting material was a moist lanthanum phosphate obtained as in Example 3 but with an excess of  $\text{PO}_4^{3-}$  ions of  $3.9 \times 10^{-3}$  mole/g of moist lanthanum phosphate with respect to the exact stoichiometry.

113.6 g of lanthanum phosphate was dispersed in 0.74 litre of deionised water with stirring and at 20°C.

26.8 g of lanthanum nitrate in solution was added to this dispersion at 20°C and with stirring, so that the  $\text{PO}_4^{3-}$ /rare earth ratio was brought to 1.

The mixture was aged for 20 minutes at 20°C.

The final concentration of this sol was 100 g/l of lanthanum phosphate and its pH was 1.36.

#### EXAMPLE 5

This example concerns the use of the sol of Example 1 for polishing.

Substrates (wafers) coated with tungsten, titanium nitride, copper or aluminium were polished.

The operating conditions were as follows:

LOGITECH PM5 CMP machine, with 4-point planarization analysis;

Pressure 2 psi ( $1.1 \times 10^4$  Pa);

Concentration of sol: 1% by weight; sol flow rate; 100 ml/min;

Table rotation rate: 33 rpm.

The results are shown in the following table:

Substrate	Al	TiN <sub>2</sub>	Cu	W
Removal rate in Å/min	5200	66	1410	21

## CLAIMS

1. A sol, characterized in that it comprises:
  - an aqueous phase;
  - particles of a phosphate of at least one rare earth selected from cerium and lanthanum;
  - 5 • an acid other than phosphoric acid, the cerium and lanthanum salts of which are soluble in water.
2. A sol as claimed in claim 1, characterized in that said acid is selected from acids with a  $pK_a$  of at least 3.
3. A sol according to claim 1 or claim 2, characterized in that said acid is selected from nitric acid, acetic acid, formic acid, citric acid and propionic acid.
4. A sol according to any one of the preceding claims, characterized in that its pH is at least 4, more particularly in the range 4 to 6.
5. A sol according to any one of the preceding claims, characterized in that the rare earth phosphate particles are constituted by elementary crystals 5 nm to 20 nm thick and in the range 25 nm to 200 nm in length.
6. A process for preparing a sol of a phosphate of at least one rare earth selected from cerium and lanthanum according to any one of claims 1 to 5, is characterized in that it comprises the following steps:
  - mixing a solution of salts of at least one of said rare earths with phosphate ions in a  $PO_4^{3-}$  /rare earth mole ratio of more than 1 with control of the pH of the reaction medium to a value of more than 2;
  - then ageing the precipitate obtained if the value of the pH of the reaction medium is in the range 2 to 6;
  - separating the precipitate from the reaction medium;
  - 25 • re-dispersing said precipitate in water;
  - adding at least one salt of said rare earth and said acid to the dispersion in a quantity such that the final  $PO_4^{3-}$  /rare earth mole ratio in the dispersion is equal to 1.

7. A process for preparing a sol of a phosphate of at least one rare earth selected from cerium and lanthanum according to any one of claims 1 to 5, characterized in that it comprises the following steps:

- continuously introducing, with stirring, a first solution of salts of at least one of said rare earths into a second solution containing phosphate ions and with an initial pH of less than 2; the phosphate ions being present in a quantity such that the  $\text{PO}_4^{3-}$ /rare earth mole ratio is more than 1;
- controlling the pH of the reaction medium to a substantially constant value of less than 2 during precipitation;
- separating the precipitate from the reaction medium;
- re-dispersing said precipitate in water;
- adding at least one salt of said rare earth and said acid to the dispersion obtained in a quantity such that the final  $\text{PO}_4^{3-}$ /rare earth mole ratio in the dispersion is 1.

8. A process according to claim 6 or claim 7, characterized in that the pH of the precipitation medium is controlled by adding a basic compound.

9. A process according to claim 8, characterized in that said basic compound is ammonium hydroxide.

10. A process according to any one of claims 6 to 9, characterized in that said phosphate ions are in the form of an ammonium phosphate solution, more particularly mono-ammonium phosphate or di-ammonium phosphate.

11. A polishing suspension, characterized in that it comprises a sol according to any one of claims 1 to 5 or a sol as obtained by the process of any one of claims 6 to 10.

12. Use of a sol according to any one of claims 1 to 5 or a sol as obtained by the process of any one of claims 6 to 10, on a substrate as an anti-corrosion agent.

13. Use of a sol according to any one of claims 1 to 5 or a sol as obtained by the process of any one of claims 6 to 10, as an anti-UV agent.

**A B S T R A C T**

**CERIUM AND/OR LANTHANUM PHOSPHATE SOL, A PROCESS FOR ITS  
PREPARATION AND USE FOR POLISHING**

**RHODIA CHIMIE**

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The invention concerns a cerium and/or lanthanum phosphate sol, a process for its preparation and its use in polishing.

The sol of the invention comprises an aqueous phase; particles of a phosphate of at least one rare earth selected from cerium and lanthanum; and an acid other than phosphoric acid the cerium and lanthanum salts of which are soluble in water.

The process for preparing this sol consists of continuously introducing a first solution of salts of at least one of said rare earths into a second solution of phosphate ions with an initial pH of less than 2; of controlling the pH of the precipitation medium during precipitation at a constant value of less than 2; of separating the precipitate from the reaction medium and of taking up the dispersion in water then adding to the dispersion obtained at least one said rare earth salt and said acid in a quantity such that the final  $\text{PO}_4^{3-}$ /rare earth mole ratio in the dispersion is 1.

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**COMBINED DECLARATION AND POWER OF ATTORNEY  
FOR UTILITY OR DESIGN PATENT APPLICATION**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**CERIUM PHOSPHATE AND/OR LANTHANUM SOL, PREPARATION METHOD AND USE FOR  
POLISHING**

the specification of which (check only one item below):

- ☐ is attached hereto.
- ☐ was filed as United States application  
Number \_\_\_\_\_ on \_\_\_\_\_  
and was amended \_\_\_\_\_ on \_\_\_\_\_ (if applicable).
- ☒ was filed as PCT international application  
Number PCT/FR00/01651 on 14 JUNE 2000  
and was amended \_\_\_\_\_ on DECEMBER 17, 2001 (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §§119 (a)-(d), 172 or 365 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. §§119(a)-(d), 172 or 365:				
COUNTRY (if PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 U.S.C. §§119, 172 or 365	
FRANCE	99/07620	16 JUNE 1999	X Yes	No
			Yes	No
			Yes	No
			Yes	No
			Yes	No



I hereby appoint the following attorneys and agent(s) to prosecute said application and to transact all business in the Patent and Trademark Office connected therewith and to file, prosecute and to transact all business in connection with international applications directed to said invention:

William L. Mathis	17,337	Eric H. Weisblatt	30,505	Bruce T. Wieder	33,815
Robert S. Swecker	19,885	James W. Peterson	26,057	Todd R. Walters	34,040
Platon N. Mandros	22,124	Teresa Stanek Rea	30,427	Ronni S. Jillions	31,979
Benton S. Duffett, Jr.	22,030	Robert E. Krebs	25,885	Harold R. Brown III	36,341
Norman H. Stepno	22,716	William C. Rowland	30,888	Allen R. Baum	36,086
Ronald L. Grudziecki	24,970	T. Gene Dillahunt	25,423	Brian P. O'Shaughnessy	32,747
Frederick G. Michaud, Jr.	26,003	Patrick C. Keane	32,858	Kenneth B. Leffler	36,075
Alan E. Kopecki	25,813	B. Jefferson Boggs, Jr.	32,344	Fred W. Hathaway	32,236
Regis E. Slutter	26,999	William H. Benz	25,952	Wendi L. Weinstein	34,456
Samuel C. Miller, III	27,360	Peter K. Skiff	31,917	Mary Ann Dillahunt	34,576
Robert G. Mukai	28,531	Richard J. McGrath	29,195	Donna M. Meuth	36,607
George A. Hovanec, Jr.	28,223	Matthew L. Schneider	32,814	Mark R. Kresloff	42,766
James A. LaBarre	28,632	Michael G. Savage	32,596		
E. Joseph Gess	28,510	Gerald F. Swiss	30,113		
R. Danny Huntington	27,903	Charles F. Wieland III	33,096		



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and:

Address all correspondence to:

Norman H. Stepno, Esquire  
BURNS, DOANE, SWECKER & MATHIS, L.L.P.  
P.O. Box 1404  
Alexandria, Virginia 22313-1404



21839

Address all telephone calls to: Teresa Stanek Rea at (703) 836-6620.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

<b>FULL NAME OF SOLE OR FIRST INVENTOR</b>	Jean-Jacques BRACONNIER
Signature	Jean-Jacques Bracconnier
Date	April 8th, 2002
Residence (City, State, Country)	Lagord, FRANCE
Citizenship	FRANCE
Mailing Address	80, rue Des Maraichers, F-17140 Lagord, FRANCE
City, State, ZIP, Country	F-17140 Lagord, FRANCE
<b>FULL NAME SECOND INVENTOR, IF ANY</b>	
Signature	
Date	
Residence (City, State, Country)	
Citizenship	
Mailing Address	
City, State, ZIP, Country	